Lattice specific heat and elastic constants for BCC, FCC and HCP lithium

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Abstract. Lithium undergoes martensitic transformations under different conditions of temperature and pressure passing, partially, from a BCC structure to a faulted close packed structure (probably a faulted 9R, HCP or FCC structure or, perhaps, a mixture of some of these phases). In this work, the lattice specific heat and elastic constants are calculated from a first principles pseudopotential for BCC, FCC and HCP lithium.

I. Introduction

The normal pressure and room temperature phase for lithium is BCC and the normal pressure and low temperature phase (below 72 K) was first described by Barret [1] as a faulted HCP structure, from X ray studies. This same author, showed that lithium cold-worked at low temperatures became FCC.

However, subsequent studies do not exclude the possibility of a more complicated packing of hexagonal layers at normal pressure and low temperatures [2,3]. Experiments with neutron diffraction performed on lithium at normal pressure and temperature of 60 K have revealed the existence of clear reflections which could be attributed to an HCP structure [4]. Simultaneously, a number of weaker reflections were observed, not all of which could be related to the HCP structure. More detailed analysis of the neutron diffraction patterns show that the 9R structure seems the most probable. However this structure does not display complete coincidence in the position and number of observed reflections either [4]. It seems that numerous stacking faults as well as admixture of the 9R phase with the 6H structure (which is a triple HCP), might be possible reasons for the discrepancies observed [4].

On the other hand, it seems that the sample does not go completely to the new phase. Only a fraction of it does [1]. Applying pressure on the sample may produce a transition from the probable 9R to FCC [5].

It is our aim in this work to calculate the contribution to the lattice specific heat of some of the different phases which could be present in a lithium sample for different conditions of temperature and pressure. We have calculated the lattice specific heat of BCC, FCC, and HCP lithium. It is our hope that this information could

be useful to experimentalists in the study of the lattice specific heat of lithium for different conditions of temperature and pressure.

II. Elastic constants and specific heat

We made our calculation using a local, first principles pseudopotential which has been useful in the prediction of properties of lithium, aluminum, sodium and potassium [6 to 13 and 23 to 25].

In previous work we employed this kind of pseudopotential with success in the calculation of the lattice specific heat of lithium [7], sodium [23,24] and aluminum [8], and of the pressure dependence of the lattice specific heat of lithium [9], and aluminum [8], and also in the calculation of the pressure dependence of the elastic constants of aluminum and lithium [10], and of the pressure dependence of the superconducting transition temperature of aluminum [11] and in the calculation of the volume dependence of the resistivity of aluminum [25]. More recently we also explored, with good results, its application in the calculation of the phonon limited resistivity of aluminum [12] and of sodium and potassium [13].

We constructed this local, first principles pseudopotential following a method proposed by Manninen *et al.* [6] who had followed some ideas of the work of Rasolt [14].

We started by calculating the displaced electron densities around a nucleus in an electron gas for lithium. This was done using the density functional formalism [15,16] and the model of the nucleus embedded into a jellium vacancy [6]. Taking into account that in the pseudopotential formulation the pseudodensity must not contain wiggles near the ion, these wiggles in the calculated density had to be removed, as we explain below.

We have used atomic units (*i.e.*, magnitude of the electron charge = electron mass = $\hbar = 1$). The energy is given in double Rydbergs.

From pseudopotential theory and linear response theory [17], the interionic potential is given by

$$\Phi(r) = \frac{Z^2}{r} \left(1 + \frac{2}{\pi Z^2} \int_0^\infty \frac{dq \, \sin(qr)\epsilon(q)[\delta n(q)]^2}{q[1 - \epsilon(q)]} \right), \tag{1}$$

where r is the separation between the two ions, Z is the charge of the metal ion, $\epsilon(q)$, is the dielectric response function of the electron gas and $\delta n(q)$ is the Fourier transform of the induced charge pseudodensity.

We calculated $\delta n(q)$, the Fourier transform of the displaced electron pseudodensity, taking the Fourier transform of the induced density [6], after smoothing. In this smoothing, the conditions that the electronic charge is conserved and that $\delta n(r)$ and $(\partial/\partial r)[\delta n(r)]$ are continuous, are imposed [6]. It is convenient to mention that in the pseudopotential formulation, the pseudodensity must not contain wiggles near the ion, and the induced density calculated from density functional theory contains

those wiggles in that region due to the orthogonalization of conduction states to core orbitals.

The unscreened pseudopotential form factor, $\nu(q)$, is related to $\delta n(q)$ by

$$\nu(q) = \frac{4\pi \delta n(q) \epsilon(q)}{q^2 [1 - \epsilon(q)]} \tag{2}$$

Eq. (2) is used to obtain an effective local pseudopotential, which in linear response will give the exact induced displaced electronic density outside the region of smoothing. In this way some of the nonlinear screening effects are included into the pair potential calculated from this pseudopotential.

The dielectric function we used satisfies by construction the compressibility theorem, which is important in connection with the interionic potential [6,14,18].

With the induced charge pseudodensity and the dielectric function already given, we used Eq. (1) to calculate the interionic potential.

From the interionic potential we calculated the phonons and associated force constants, using the harmonic approximation.

From the tensor force model and using notation of reference [19], the force matrix, Φ_{ij}, is defined as the force on the origin atom in the i direction when atom S moves one unit distance in the j direction. This force matrix is symmetric and it is denoted by

$$\Phi_{ij}^{(S)} = \begin{pmatrix} \alpha_1^S & \beta_3^S & \beta_2^S \\ \beta_3^S & \alpha_2^S & \beta_1^S \\ \beta_2^S & \beta_1^S & \alpha_3^S \end{pmatrix} \tag{3}$$

The point S is one of a set of points according to the symmetry of the lattice. This set of points is denoted by S, where $S = 1, 2, 3$, etc., corresponding to every shell of neighbors. The force matrices of the other members of the set consist of rearrangements of the same set of force constants.

For cubic symmetry the elastic constants, C_{11}, C_{44}, C_{12} are given by [19]

$$aC_{11} = 8\tau \sum_S \frac{n^S}{48} \sum_j \left(h_j^S \right)^2 \alpha_j^S$$

$$aC_{44} = 4\tau \sum_S \frac{n^S}{48} \sum_j \left[\left(h_{j+1}^S \right)^2 + \left(h_{j+2}^S \right)^2 \right] \alpha_j^S$$

$$a \left(C_{11} + C_{44} \right) = 16\tau \sum_S \frac{n^S}{48} \sum_j h_{j+1}^S \cdot h_{j+2}^S \beta_j^S \tag{4}$$

where a is the lattice constant, n^S is the number of lattice points for neighbor shell S; h_j^S corresponds to three non-negative integers such that $h_1 \geq h_2 \geq h_3$ and the

coordinates of a point in shell S are $h_1 a/2$, $h_2 a/2$, $h_3 a/2$. For FCC $\tau = 1$ and for BCC $\tau = 1/2$.

For cubic symmetry the relations between the force constants of the tensor force model and the axially symmetric model are [19]

$$\alpha_1^S = C_B(S) + \left(\frac{h_1^2}{h^2}\right) k_1(S) \qquad \beta_1^S = \left(\frac{h_2 h_3}{h^2}\right) k_1(S)$$

$$\alpha_2^S = C_B(S) + \left(\frac{h_2^2}{h^2}\right) k_1(S) \qquad \beta_2^S = \left(\frac{h_3 h_1}{h^2}\right) k_1(S) \qquad (5)$$

$$\alpha_3^S = C_B(S) + \left(\frac{h_2^3}{h^2}\right) k_1(S) \qquad \beta_3^S = \left(\frac{h_1 h_2}{h^2}\right) k_1(S)$$

where $h^2 = h_1^2 + h_2^2 + h_3^2$, and $k_1(S)$ and $C_B(S)$ are the two force constants of the axially symmetric model for the S-th shell of neighbors [19].

We could relate easily the force constants $k_1(S)$ and $C_B(S)$ to the derivatives of the interionic potential and we obtained

$$k_1(S) = \left[\frac{d^2 V(r)}{dr^2} - \frac{1}{r}\frac{dV(r)}{dr}\right]_{(S)} \qquad (6)$$

and

$$C_B(S) = \left[\frac{1}{r}\frac{dV(r)}{dr}\right]_{(S)} \qquad (7)$$

In this way, from the interionic potential $V(r)$, we could find $k_1(S)$ and $C_B(S)$ and using equations (4) and (5) we could calculate the elastic constants for BCC and FCC structures. We had a good convergence using 12 neighbor shells.

For the HCP structure we had a good convergence with four neighbor shells. For this case the elastic constants are [20]

$$C_{11} = \sqrt{3}\frac{3\alpha - A_1 - L}{2c} \qquad (8)$$

$$L = \frac{(2B_2 + G_2 + 3G_1)(3B_1 + B_2 + 8G_2) + 2G_2(3B_1 + B_2)}{3(B_1 + B_2 + G_1 + G_2)} \qquad (9)$$

$$C_{33} = \frac{c}{\sqrt{3}a^2}\left[-3(B_3 + B_3) + 4\delta\right] \qquad (10)$$

$$C_{44} = \frac{-2}{\sqrt{3}c}\left[3A_2 + B_3 + 4G_3\right] \qquad (11)$$

$$C_{12} = \frac{-1}{\sqrt{3}c}\left[3(\alpha - 3A_1) - B_1 - B_2 - 12G_1 - 4G_2 + P\right] + C_{11} \qquad (12)$$

$$P = \frac{\left(B_1 - B_2 - 2G_1 + 2G_2\right)^2}{B_1 + B_2 + G_1 + G_2} \qquad (13)$$

$$C_{13} = \frac{2}{a}\left(2G_4 - B_4\right) - C_{44} \qquad (14)$$

In the case of an ideal HCP structure, $c/a = \sqrt{8/3}$.
Finally

$\alpha = -[k_1(1) + C_B(1)];$ $A_1 = A_2 = C_B(1);$ $A_3 = 0;$

$B_1 = C_B(2);$ $B_2 = \frac{1}{3}[k_1(2) + 3C_B(2)];$ $B_3 = 2B_2 - B_1;$

$B_4 = \sqrt{2}(B_2 - B_1);$ $G_1 = C_B(3);$ $G_2 = \frac{1}{3}[2k_1(3) + 3C_B(3)];$

$G_3 = \frac{1}{2}(G_1 + G_2);$ $G_4 = \frac{(G_2 - G_1)}{\sqrt{2}};$ $\delta = -[k_1(4) + C_B(4)].$

Again, from the interionic potential we could find $k_1(S)$ and $C_B(S)$ and, from these, the corresponding elastic constants for HCP.

To calculate the phonon frequency distribution, $F(\nu)$, from the force constants obtained in the phonon dispersion curve, we followed the method of Gilat and Raubenheimer [21].

From $F(\nu)$, the specific heat is calculated numerically by the integral

$$C_\nu = \frac{\partial\langle E\rangle}{\partial T} = k_B \int_0^{\nu_m} d\nu \left(\frac{\beta h\nu}{2}\right)^2 \frac{F(\nu)}{\sinh(\frac{1}{2}\beta h\nu)}, \qquad (15)$$

where $\langle E\rangle$ is the average of the internal energy, T is the temperature and ν_m is the maximum phonon frequency.

In Fig. 1 the resulting phonon spectra for BCC, FCC and HCP are shown. The phonon spectra were obtained using first the harmonic approximation to get the force constants and the using the method of Gilat and Raubenheimer [21].

Our calculated phonon spectra for low temperature are similar to those obtained by Punz and Hafner [22]; however, these authors did not report any calculation of the lattice specific heat. These authors used an optimized Harrison pseudopotential and the dielectric function of Vashista and Singwi. This dielectric function does not satisfy the compressibility theorem which is important in connection with the interionic potential, as we have already mentioned.

The results for the lattice specific heats for BCC, FCC and HCP lithium are shown in Fig. (2). We can see that the results for BCC and FCC are, practically, identical. This could be expected because of the similarity of the phonon spectra for these
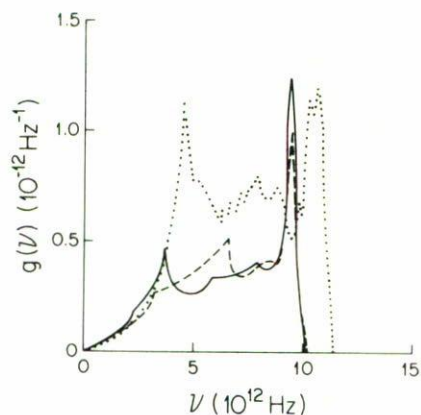
FIGURE 1. Calculated Phonon spectrum for lithium with different structures. For BCC: —; for FCC: - - -; for HCP: ⋯. The calculations were made at a temperature of 78 K.
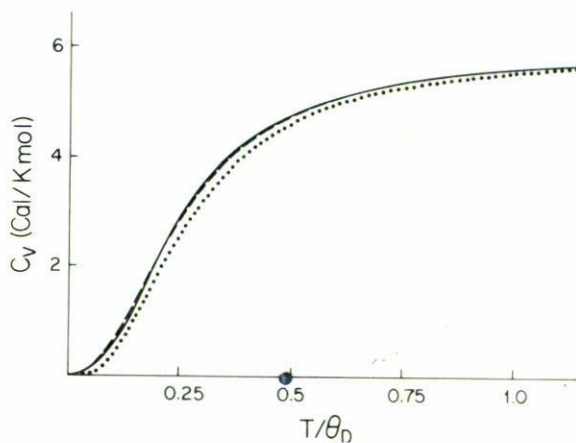

FIGURE 2. Constant volume lattice specific heat of lithium as function of the temperature for different structures. Result of this calculation for BCC: —; result for FCC; - - -; and for HCP: ⋯

	C_{44}	C_{11}	C_{12}	C_{33}	C_{13}
BCC	0.069	0.137	0.115		
FCC	0.078	0.172	0.138		
HCP	0.059	0.429	0.188	0.359	0.083

TABLE I. Elastic constants of BCC, FCC and HCP lithium. The units are 10^{12} dynes/cm². The calculation is for 78 K. Lithium undergoes a martensitic transformation below 80 K to a probable FCC or to an HCP structure.

structures (Fig. 1). We could not find experimental results for the specific heat for one phase alone of lithium below 80 K.

Our calculated elastic constants, for BCC, FCC and HCP lithium for temperatures below 80 K are shown in Table I.

Acknowledgements

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Resumen. El litio pasa por una transformación martensítica bajo diferentes condiciones de temperatura y presión cambiando parcialmente de una estructura BCC a una estructura de empaquetamiento compacto imperfecta (probablemente a una estructura 9R imperfecta, HCP o FCC o quiza, a una mezcla de alguna de estas fases). En este trabajo, se calculan el calor específico de la red y las constantes elásticas a partir de un pseudopotential de primeros principios, para litio con estructuras BCC, FCC y HCP.